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ATIKOKAN TGS COAL ASH DISPOSAL STUDY: LIGNITE COAL ASH LEACHATE CHEMISTRY

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ABSTRACT

As part of the Atikokan TGS coal ash disposal project, batch equilibrium tests were carried out to study the leaching behaviour of Atikokan TGS lignite coal ash under a range of simulated disposal conditions. Nine different combinations of coal ash with deionized water were used to generate a variety of leachates. Chemical analyses of the series of fly ash leachates show that with an increase in solution to solid ratio, most constituents decrease in concentration. The addition of a small portion of bottom ash to fly ash resulted in similar or lower quantities of leachate constituents when compared to a fly ash leachate developed with the same water content. These relationships could be useful when attempting to reduce generated levels of elements of environmental concern in disposal site porewater.

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To Mr. M.J. Northfield
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A7A2

**ATIKOKAN TGS COAL ASH DISPOSAL STUDY:
LIGNITE COAL ASH LEACHATE CHEMISTRY**

1.0 INTRODUCTION

As part of the Atikokan TGS coal ash disposal project, a number of batch equilibrium tests were carried out using Atikokan TGS lignite coal ash. The objective of this investigation is to simulate a range of disposal conditions in order to analyze the chemistry of the generated porewaters.

The major portion of coal ash produced at the Atikokan TGS is fly ash (80-85%), while bottom ash comprises the remainder (15-20%). For this reason, the majority of leachate samples were prepared using only fly ash as the solid portion. One specimen was developed from bottom ash exclusively. In addition, to discover the effect that a particular combination of bottom ash with fly ash would have on leachate chemistry, an ash sample was prepared proportional to coal ash production - 80% fly ash with 20% bottom ash by weight.

The chemical characteristics of the generated leachates are largely dependent on the ash bulk chemistry. Therefore, bulk elemental analyses of both Atikokan TGS coal fly ash and a lignite coal bottom ash are included which list the elements that comprise these materials.

To calculate geochemical reactions associated with leachate generation, a computer program known as PHREEQE (Parkhurst, Thorstenson and Plummer, 1980) was utilized.

2.0 MATERIAL AND METHODS

2.1 Bulk Elemental Analyses

The coal ash used for the batch equilibrium tests is a by-product of Western Canadian lignite coal burned at the Atikokan Thermal Generating Station. The results from bulk elemental analyses of Atikokan coal fly ash and lignite coal bottom ash are presented in Table 1 (PEMRC, 1988) and Table 2 (Dodd, 1979), respectively. Both types of ash are predominantly composed of silicon (as SiO_2), aluminum (as Al_2O_3) and calcium oxide with moderate amounts of sodium, iron and magnesium. When plotted on the compositional field diagram (Figure 1) proposed by Roy and Griffin (1982), Atikokan coal ash falls in an area known as modic.

2.2 Laboratory Procedures

To evaluate a range of disposal conditions and the associated porewaters, nine different combinations of Atikokan coal ash with deionized water were involved in this study (refer to Table 3). Static equilibrium batch tests were conducted on lignite fly ash using seven different solution to solid ratios (0.5:1, 1:1, 2:1, 3:1, 5:1, 7.5:1 and 10:1). In addition, deionized water was combined with a sample of Atikokan bottom ash at 0.5:1 and a blend of fly ash (80%) with bottom ash (20%) was prepared at a 1:1 solution to solid ratio. The nine different mixtures were left to equilibrate for 120 hours under static conditions at a temperature of 21°C. At this point, each sample was centrifuged to separate the liquid from the ash and the extracted leachate was passed through a 0.45 *um* filter to prepare for chemical analysis. The results obtained from the analyses are listed in Table 4.

2.3 Geochemical Modelling

The computer program PHREEQE by Parkhurst, Thorstenson and Plummer of the U.S. Geological Survey, was designed to model geochemical reactions. This Fortran IV program will calculate solution speciation and saturation states of the aqueous phase with respect to various mineral phases based on an ion pairing aqueous model. Analytical concentrations of the elements, pH and temperature are used as input and if redox reactions are to be considered, then electron activity values (pE) are required. In this exercise, PHREEQE was utilized to calculate the distribution of aqueous species in the generated ash leachates.

3.0 RESULTS AND DISCUSSION

When comparing all nine leachates generated from Atikokan coal ash, the fly ash leachate prepared at 0.5:1 generally contains the highest quantities of analyzed constituents, while the bottom ash sample yields the lowest values. The exceptions to this trend are calcium, magnesium and strontium which were detected at much higher levels in the bottom ash leachate than in all the other leachate samples.

The series of fly ash leachate samples are characterized by element concentrations which gradually decrease as the solution to solid ratio increases. Calcium, however, behaves in a reverse fashion.

To provide an explanation for the escalating calcium concentrations, solution chemistries of the fly ash leachates were modelled. The majority of calcium in aqueous form is distributed between three species - Ca^{2+}, $CaCO_3$ and $CaSO_4$. For simplification, the dominant sulphate and carbonate species of the two extreme solutions (0.5:1 and 10:1) are listed in Table 6. At the low moisture content (0.5:1), $NaSO_4^-$ and $NaCO_3^-$ are the dominant species, SO_4^{2-} and CO_3^{2-} are second while $CaSO_4$ and $CaCO_3$ rank third. However, when the solution to solid ratio is 10:1, the order changes as follows: the dominant species are SO_4^{2-} and CO_3^{2-} followed by $CaSO_4$ and $CaCO_3$ and thirdly $NaSO_4^-$ and $NaCO_3^-$. These relationships show that in order to maintain equilibrium, calcium (Ca^{2+}) values are low at 0.5:1 and progressively increase with additional moisture content.

It is apparent that the addition of a small portion of bottom ash to fly ash will decrease the concentration of most leachate constituents. For example, elements are present at similar or lower quantities in leachate produced from an ash blend (fly ash\bottom ash) when compared to fly ash leachate produced at the same moisture ratio (1:1). The percent differences of a number of constituents are calculated and displayed in Table 5. A significant difference to note is the 27% reduction of arsenic in the blend leachate.

These results verify that chemical constituents in bottom ash are not as readily dissolved as those in fly ash for a number of morphological reasons. Bottom ash is in a vitrified state after the combustion process and has a lower surface area per unit weight than silt-size fly ash particles. In addition, elements tend to be uniformly distributed throughout a bottom ash particle while a fly ash particle carries a concentration of elements on its surface (EPS, 1986). Therefore, elements in fly ash are more readily accessible for leaching than those elements fixed in the matrices of bottom ash.

4.0 SUMMARY

In summary, the solution to solid ratio apparently has an effect on the resulting constituent concentrations. With regard to fly ash leachate, in general, the highest element quantities are associated with the lowest moisture content. The addition of bottom ash to fly ash also affects leachate quality by reducing the levels of most constituents. These relationships could perhaps be useful when attempting to lower generated levels of elements of environmental concern in disposal site porewater.

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5.0 REFERENCES

1. Dodd, D.J.R., 1979. Estimation of lignite bottom ash sluice water composition. OHRD #79-366-K.

2. Environmental Protection Service, 1986. Contaminant solubilization in bench-scale recirculating ash transport systems. EPS 3/PG/5.

3. Parkhurst, D.L., D.C. Thorstenson, and L.N. Plummer, 1985. PHREEQE - A Computer Program for Geochemical Calculations. U.S. Geological Survey, Water Resources Investigations 80-96, NTIS Tech. Report PB81-167801, 1980, revised 1985.

4. PEMRC, 1988. Report of research works on fly ashes from power plants of Ontario Hydro, Canada in respect of their utilization for producing emulsifying agent. Power Engineering Measurement and Research Centre "Energopomiar", Dept. Power Plant Waste Management Technology, Katowic, Poland.

5. Roy, W.R., and R.A. Griffin, 1982. A proposed classification system for coal fly ash in multidisciplinary research. J. Environ. Qual. 11:563-568.

TABLE 1: BULK ELEMENTAL ANALYSIS OF ATIKOKAN TGS FLY ASH

Element	(mg/kg)
Aluminum	109080
Arsenic	24.2
Barium	8600
Cadmium	< 2
Calcium	109566
Chloride	50
Chromium	78
Cobalt	< 10
Copper	74
Fluoride	360
Iron	38451
Lead	30
Magnesium	20381
Manganese	183
Molybdenum	14
Nickel	86
Phosphorous	2925
Potassium	5230
Selenium	1.6
Silicon	196187
Sodium	54904
Strontium	1750
Sulphur	7608
Titanium	4736
Vanadium	88
Zinc	100

TABLE 2: BULK ELEMENTAL ANALYSIS OF LIGNITE COAL BOTTOM ASH

Element	(mg/kg)
Aluminum	100000
Arsenic	8
Barium	11000
Boron	1580
Cadmium	<10
Calcium	90000
Chromium	150
Cobalt	6
Copper	520
Iron	33000
Lead	<15
Magnesium	19000
Manganese	120
Mercury	20
Molybdenum	<20
Nickel	22
Phosphorus	1510
Potassium	2000
Selenium	4
Silicon	206000
Silver	<0.5
Sodium	49000
Strontium	4400
Sulphur	2000
Titanium	5200
Uranium	21
Vanadium	45
Zinc	11

Note: from test burns of Bienfait lignite coal at the Canadian Combustion Research Lab

TABLE 3: BATCH EQUILIBRIUM TEST SAMPLE DESCRIPTION

Sample	Atikokan Coal Ash	solution:solid
#1	100% fly ash	0.5:1
#2	100% fly ash	1:1
#3	100% fly ash	2:1
#4	100% fly ash	3:1
#5	100% fly ash	5:1
#6	100% fly ash	7.5:1
#7	100% fly ash	10:1
#8	100% bottom ash	0.5:1
#9	80% fly ash 20% bottom ash	1:1

TABLE 4: CHEMICAL ANALYSIS OF ATIKOKAN COAL ASH LEACHATE (mg/L)

Constituent *	0.5:1 (fly ash)	1:1 (fly ash)	2:1 (fly ash)	3:1 (fly ash)	5:1 (fly ash)	7.5:1 (fly ash)	10:1 (fly ash)	0.5:1 (bot.ash)	1:1 (blend)
Arsenic	1.28	0.213	0.015	0.009	0.006	0.004	0.003	0.005	0.156
Barium	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Boron	68.0	23.0	14.2	11.1	7.4	6.1	5.4	23.0	20.0
Cadmium	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Calcium	2	12	52	56	64	78	89	540	14
Chloride	122.0	32.3	18.8	12.3	6.7	4.6	3.8	2.9	33.0
Chromium	5.0	2.7	1.2	0.89	0.64	0.42	0.30	<0.01	2.26
Copper	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fluoride	44.3	25.6	11.4	9.3	6.2	4.6	4.3	3.3	23.5
Iron	0.10	0.04	<0.05	<0.05	<0.05	<0.05	<0.05	<0.01	0.04
Lead	<0.03	<0.03	0.16	0.15	0.12	0.11	0.10	0.05	<0.03
Magnesium	<0.005	<0.005	0.012	0.013	0.014	0.016	0.018	0.79	<0.005
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mercury	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Nitrate	51.7	21.8	8.3	4.7	3.1	2.4	1.7	0.3	17.8
Nitrite	0.51	0.26	0.05	0.05	<0.01	<0.01	<0.01	0.04	0.18
Potassium	85.0	26.0	17.2	11.8	7.2	4.9	3.8	2.1	27.0
Selenium	3.47	1.46	0.46	0.40	0.37	0.32	0.33	0.005	1.28
Silver	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sodium	8000	3400	1485	1090	712	468	348	176	2900
Strontium	2.1	4.6	12.6	13.6	12.7	12.1	11.8	19.0	6.2
Sulphate	11200	4790	3190	2035	1140	832	601	1570	4100
Uranium	<0.2	<0.2	1.5	1.0	1.1	<0.5	<0.5	<0.2	<0.2
Zinc	<0.01	<0.01	0.02	0.02	0.02	0.02	<0.02	<0.01	<0.01
alkalinity	6800	2500	1280	1040	847	636	529	93	2200
pH	12.7	12.2	12.1	11.7	11.6	11.5	11.5	8.97	12.1
conductivity (mmho/cm)	24	12	8.6	6.4	4.2	3.2	2.6	2.2	11

* - average values

TABLE 5: COMPARISON OF FLY ASH LEACHATE TO BLEND LEACHATE

Constituent *	A fly ash (1:1) (mg/L)	B blend (1:1) (mg/L)	A ---> B % difference
Arsenic	0.213	0.156	-27
Boron	23	20	-13
Calcium	12	14	+17
Chlorine	32.3	33	+2
Chromium	2.7	2.26	-16
Fluoride	25.6	23.5	-8
Iron	0.04	0.04	0
Nitrate	21.8	17.8	-18
Nitrite	0.26	0.18	-31
Potassium	26	27	+4
Selenium	1.46	1.28	-12
Sodium	3400	2900	-15
Strontium	4.6	6.2	+35
Sulphate	4790	4100	-14

* - constituents not listed are at levels below their detection limit

TABLE 6: DOMINANT SPECIES WITH ASSOCIATED ION ACTIVITIES

RATIO	SULPHATES	CARBONATES	SODIUM	CALCIUM
0.5:1	$NaSO_4^-$ (1.9D-02) SO_4^{2-} (1.7D-02) $CaSO_4$ (1.4D-05)	$NaCO_3^-$ (1.5D-02) CO_3^{2-} (3.6D-03) $CaCO_3$ (2.0D-05)	Na^+ (2.2D-01)	Ca^{2+} (4.0D-06)
10:1	SO_4^{2-} (3.0D-03) $CaSO_4$ (3.4D-04) $NaSO_4^-$ (1.9D-04)	CO_3^{2-} (1.1D-03) $CaCO_3$ (8.5D-04) $NaCO_3^-$ (2.5D-04)	Na^+ (1.3D-02)	Ca^{2+} (5.6D-04)

FIGURE 1: COAL FLY ASH CLASSIFICATION SCHEME